

# Stress-strain relations in bulk metallic glasses and colloidal dispersions

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A comparison is made between the nonlinear rheological response of bulk metallic glass formers and of colloidal dispersions. Stress-strain curves measured after switch-on of constant deformation rates are analyzed quantitatively using a schematic model of mode coupling theory generalized to homogeneous and incompressible flows. A mapping between metallic and dispersion rheology is possible when stresses are rescaled by an entropic scale, accumulated strains by geometrical factors, and rates by the intrinsic relaxation time. Exploiting this similarity and the possibility to directly observe individual colloidal particles, we investigate the structural distortions in the colloidal system using confocal microscopy. The distortions exhibit the (from elasticity theory) expected quadrupolar but also a strong isotropic component.

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The nonlinear rheological response of melts and complex fluids directly relates to the internal motion of the constituents. Flow causes affine motion on average, but also affects the fluctuations of particle positions and momenta. This non-affine motion changes the diffusive properties of the particles [1, 2], affects the stress fluctuations and distributions [3], and generally determines the macroscopic response of the material [4]. The latter is strongly affected because solid structures, either stable or metastable are broken up and the system is fluidized. Rheology is thus perfectly suited to investigate glass forming materials.

Bulk metallic glasses exhibit unique mechanical properties of technological importance, and have therefore been the focus of intense investigations [5]. Their microscopic deformation modes, however, remain incompletely understood [6]. While metallic melts deform plastically on the atomic scale, which determines their casting properties, in the arrested state, they typically fail as brittle materials by shear banding.

The intrinsic entities of deformation in amorphous metals under flow are still unknown. Their investigation is, however, possible using colloidal dispersions. This opens the way for experiments such as (confocal) microscopy [1, 2, 7, 8], echo-diffusing wave spectroscopy [9], and scattering techniques [10] to observe the particle motions and arrangements under flow. The present letter first establishes a close link between metal and dispersion rheology by a quantitative combined modeling of their transient stress response. The rheological response is then related to the strain-induced structural response by observing the local shear-induced distortions of the colloid packing via microscopy and simulations.

Theoretical progress on glass rheology often proceeds via considering specific choices of local particle moves and deducing the macroscopic response from them. Free volume and shear-transformation-zone theory are two prominent approaches [11, 12], and recent progress concerns long-ranged couplings between individual excitations [13]. Generally, excitations of quadrupolar angular dependence are considered based on arguments from continuum elasticity theory. Mode coupling theory (MCT), on the other hand, addresses the problem starting from a microscopic description of the quiescent structural relaxation in a supercooled liquid [14], generalizing it to flow-driven systems [15]. The description relies on (low-order) correlation functions which capture the average behavior of unspecified deformation entities. Non-Markovian effects play an important role, although they are only added occasionally in other approaches, e.g. to capture spectral broadening [16]. The spatial structures involved in the wavevector dependent memory kernels of MCT reveal a localization of particles in cooperatively formed cages. The localization length quantifies Lindemann's insight that in a solid just at its limit of stability particles rattle around their average sites by about a tenth of the average spacing [17].

The present study is aimed at metallic and colloidal fluids close to their glass transitions, where non-Markovian contributions to the dynamics are most pronounced. We investigate whether the averaged correlation-function description of the effects of plastic deformations on structural relaxation can rationalize the behaviors of two widely different kinds of liquids. While the dispersion is close to its MCT glass transition, the metal alloy is below the  $T_c$  of MCT [18]. Our work thus addresses the

question about the generic flow effects in an averaged correlation function description of the structural relaxation.

We start from the generalized Green-Kubo relation for the transient (deviatoric) stress tensor  $\sigma(t)$  [15]. For an incompressible, homogeneous, and constant strain rate tensor it becomes [19]:

$$\sigma(t, \dot{\gamma}) = \int_0^t dt' \partial \mathbf{B}(t-t') / \partial t g(t-t', [\mathbf{B}]). \quad (1)$$

It yields the resulting stress after switch-on of flow. The Finger tensor  $\mathbf{B}$  describes the affine straining of particle separations. The stress correlation function  $g(t, [\mathbf{B}])$  captures the response of the material. Equation (1) entails the principles of locality, causality, and material objectivity (the rheological response is independent of arbitrary, including time-dependent, global rotations) [15, 20].

MCT-ITT captures the internal and non-affine particle motion using transient density correlation functions. Because of the strong local coupling of the structural dynamics [14], a single correlation function  $\Phi(t, [I])$  can be used. The resulting schematic model [21] states that transient stress fluctuations decay by particle interactions which leads to a quadratic relation

$$g(t, [\mathbf{B}]) = v_\sigma(I(t)) \Phi^2(t, [I]). \quad (2)$$

Strain enters the model via the invariants of the Finger tensor, which combine to the accumulated strain  $I(t)$  [19]. Incompressibility leads to a quadratic expansion  $I(t) = (\dot{\gamma}t)^2 + \dots$  with a nominal strain rate  $\dot{\gamma}$ , which suffices in the cases considered here, where the steady states are reached for strains around 0.3. (Two different deformation geometries will be considered: simple shear and uniaxial compression, resulting in  $\dot{\gamma} = \dot{\gamma}_s$  and  $\dot{\gamma} = \sqrt{3}\dot{\gamma}_u$ , respectively.) The stress-density coupling vertex  $v_\sigma(I(t))$  gives the elasticity stored in the structure. Affine deformations destroy it gradually, which suggests that  $v_\sigma(I(t))$  decreases with increasing strain [21]:

$$v_\sigma(I(t)) = v_\sigma^* (1 - I(t)/\gamma_*^2) \exp[-I(t)/\gamma_{**}^2]. \quad (3)$$

The stress-scale is set by  $v_\sigma^*$ . In 'repulsive glass formers', where the harsh repulsive interactions dominate the structure [22, 23], microscopic MCT finds it to be of entropic nature [21]. For hard sphere systems at the glass transition,  $v_\sigma^*$  scales with  $k_B T/R^3$ , viz. the thermal energy per particle volume. Equation (3) includes two characteristic strain values. They have been calculated for hard disks in two dimensions [21], but serve as fitting parameters in the schematic model. The value of  $\gamma_*$  indicates when stress fluctuations become anti-correlated,  $g([I] > \gamma_*) < 0$  [2]. The strain  $\gamma_{**}$  corresponds to the limit over which stresses can remain correlated in a glass. In fluid states, plastic decay in  $\Phi(t)$  cuts off the transient stress relaxation earlier. The two strains  $\gamma_*$ ,  $\gamma_{**}$  are material constants connected to the melting/cage-breaking process [14, 17].

The schematic model is completed by an equation of motion for the density correlator  $\Phi(t, [I])$ , which contains a memory kernel describing non-Markovian friction. It models the feedback mechanism in supercooled liquids that structural rearrangements slow down because of higher friction, which itself grows because of slower structural rearrangements. This leads to the idealized glass transition of MCT [14]. We use the schematic  $F_{12}^{(\dot{\gamma})}$  model [21], which includes the suppression of memory by flow and has been used frequently.

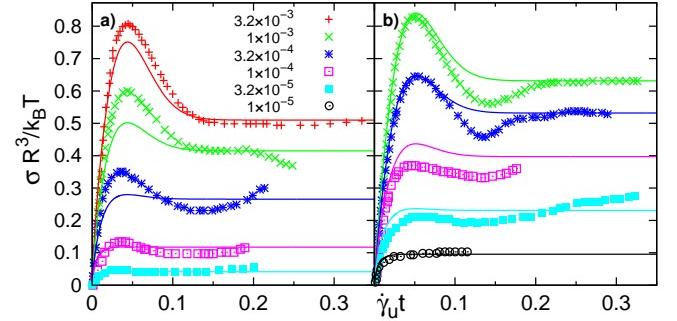


FIG. 1. Stress vs strain curves of Vitreloy 1 ( $\sigma = \sigma_{xx}$ , symbols) for different rates, from Ref. [24], with schematic MCT fits (lines; parameters in Tab. I); the legend in (a) gives the compression rates  $\dot{\gamma}_u$  in  $s^{-1}$ . Panel (a) shows data at the glass transition  $T = T_g = 623K$ , and panel (b) at  $T = 613K$ .

In the following, we first show that the model describes compressional stresses  $\sigma_{xx}$  measured on the bulk metallic glass former  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  (Vitreloy 1) in the vicinity of its glass transition temperature  $T_g$  [24]. Then we use the model to map the Vitreloy data to shear stress-strain curves measured in colloidal dispersions of thermosensitive PNIPAM microgels immersed in water, at packing fraction  $\phi = 0.60$  close to their colloidal glass transition [25]. Finally, we investigate the strain-induced changes in the local structure by observing the motion of the colloids by confocal microscopy.

Figure 1 shows stress-strain relations of Vitreloy 1 for two temperatures at and below  $T_g \approx 623K$  [24]. At first, the stress increases linearly with accumulated strain,  $\sigma_{xx} = 2G_\infty \dot{\gamma}_u t$ , which allows the easy identification of the elastic shear modulus  $G_\infty$ . According to MCT, stress and  $G_\infty$  are scaled in units of  $k_B T/R^3$ , with  $R$  an appropriate particle radius. We chose the covalent radius of the majority element, i.e.  $R_{Zr}=175pm$ . This gives  $G_\infty \approx 14k_B T/R^3$ , which describes an increase of the stress up to order unity in rescaled units. The flow rate becomes relevant when the Weissenberg number  $Pe = \dot{\gamma}t$  indicates that the inverse rate and the internal relaxation time become comparable. We estimate the latter from the model fits by the Maxwell relation  $\tau = \eta_0/G_\infty$  with the Newtonian viscosity  $\eta_0$ . For  $Pe > 1$ , a clear maximum in stress develops (Fig. 2) because stress fluctuations become anti-correlated for larger strains. The

stress-correlation function  $g(t, [\mathbf{B}])$  in Eq. (2) becomes negative, and the integral, which gives the stress according to Eq. (1), decreases. The maximum lies at strain  $\gamma_*$ . Increasing Pe, the overshoot increases and in some curves a shallow minimum develops before at large strains the stress approaches its value on the flow-curve. The minimum is absent in the schematic model, where  $\gamma_{**}$  gives the strain when the flow-curve asymptote is monotonically reached [21].

Metal	$v_\sigma^* [k_b T / R_{Zr}^3]$	$\gamma_*$	$\gamma_{**}$
$T = 613K$	162	0.0894	0.122
$T = 623K$	160	0.0762	0.115
Colloids	$v_\sigma^* [k_b T / R_H^3]$	$\langle \gamma_* \rangle$	$\langle \gamma_{**} \rangle$
$\phi = 0.60$	90	0.10	0.129

TABLE I. Parameters in Eq. (3) for the fits to the metallic glass Vitreloy 1 and colloidal dispersion PNiPAM; mean values given of the strains; see [26] for  $F_{12}^{(\dot{\gamma})}$  parameters.

According to MCT, the rescaled stresses in metallic melts and colloidal solutions should obey similar relations with accumulated strain even though the absolute values differ by about nine orders of magnitude [27, 28]. Rescaled by  $k_B T / R^3$ , with  $R_{Zr}=175\text{pm}$  in Vitreloy 1 and  $R_H=90\text{nm}$  for the colloidal microgels, data from the two systems can be compared quantitatively. This is shown in Fig. 2, where the rescaled stresses are shown as a function of time rescaled by the strain rate  $\dot{\gamma}$ . The different geometry, uniaxial for the metallic versus shear for the colloidal fluid, enters the relation between the true and the nominal strain rate :  $\dot{\gamma} = \dot{\gamma}_s$  and  $\dot{\gamma} = \sqrt{3}\dot{\gamma}_u$ . The characteristic strain of the position of the stress-overshoot for both systems then almost agrees. This implies, following Lindemann's insight, that the local cages which freeze-in at the structural glass transition are comparable in soft and hard systems, if rescaled variables are used. Rescaling the strain rate leads to the Weissenberg number  $\text{Pe} = \dot{\gamma}\tau$ . Its values indeed indicate that both systems are driven with comparable rescaled rates, with the colloid experiment covering a broader but overlapping range in Pe. The similarity in the stress vs strain curves shown in Fig. 2 is recovered in the similarity of the parameters obtained when the schematic model is fitted to the data (Tab. I). Over the broader range in effective shear rates in the colloid experiment, slight drifts in the model parameters are visible which are not required for the metallic data [21].

To reveal the microscopic origins of the stress-strain curves we investigate the local structural distortions. The universality in the metal and colloid rheology allows us to generalize findings in colloidal dispersions. Using confocal microscopy we can observe individual particles and hence their rearrangements under flow, and the affine and non-affine motion can be separated. Figure 3 shows pair-correlation functions [29] determined at four strains

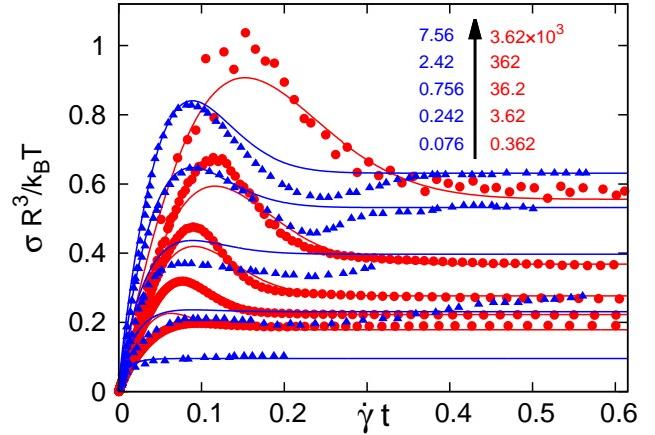


FIG. 2. Comparison of stress vs strain measurements for varying strain rates in a metallic melt ( $\sigma = \sigma_{xx}$ , blue triangles) and a colloidal dispersion ( $\sigma = \sigma_{xy}$ , red circles). The metallic glass data is taken from Fig. 1 b) at  $T = 613K < T_g$ , and the colloidal data of a fluid state is taken from Ref. [21]. Strain rates, converted to and listed as Weissenberg numbers, increase along the arrow. Solid lines are MCT fits with the schematic model for the parameters in Tab. I.

after switch-on of shear in PMMA-colloids (average radius  $R=780\text{nm}$ , polydispersity  $\approx 6\%$ ) slightly below their glass transition packing fraction ( $\phi = 0.565$  relative to  $\phi_c = 0.58$  [10]; same samples and confocal microscopy as in [30]). The shear distortion  $g(\mathbf{r}) - g^{\text{eq}}(r)$ , i.e. the difference between the sheared and equilibrium pair distribution functions, exhibits an anisotropic quadrupolar and an isotropic angular contribution, which are obtained by angular averaging with the appropriate spherical functions [31]. The quadrupolar term relates to the shear stress and becomes more pronounced with strain; this is consistent with a very weak shear stress overshoot measured in comparable PMMA systems [32]. It describes a shift of the neighbor peak to smaller (larger)  $r$  along the compressional (extensional) axis. The isotropic distortion in  $g(\mathbf{r}) - g^{\text{eq}}(r)$  is unexpected from continuum elasticity, yet, for distances connected to the local caging, it is comparable to the quadrupolar distortion in magnitude. It corresponds to a shift of the neighbor peak towards smaller distances  $r$ , which we interpret as a local compression of the system. The very small compressibility of the system suggests a strong increase of the diagonal parts of the stress tensor which give the pressure; it has been linked to shear banding [33, 34], although flow remains homogeneous in our study. This could be caused by the different transient evolution (shear stress overshoot vs monotonous pressure increase).

To support our finding of strong local compressional effects under shear we turn to simulations. A two-dimensional binary mixture of hard disks in a glassy state slightly above its MCT glass transition packing fraction

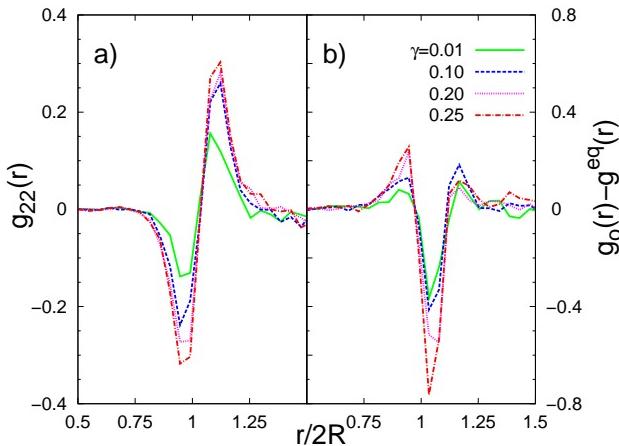


FIG. 3. Distortions of the pair correlation function,  $g(\mathbf{r}) - g^{eq}(r)$  as a function of distance  $r$ : Quadrupolar  $g_{22}$  in panel (a), isotropic  $g_0 - g^{eq}$  in panel (b), for strains as labeled after switch-on of shear in PMMA colloids with average radius  $R$ ; the shear rate corresponds to  $Pe \approx 79$ .

( $\phi = 0.81$  relative to  $\phi_c = 0.80$  [35]) exhibits stress-strain curves which share all the discussed features of the experimental data [21]. Because the neighbor peak is fixed at the diameter  $d$  for hard spheres and cannot move inward, the observed compression should correspond to an increase in the contact value. It also determines all elements of the stress tensor in the Virial-law:

$$\boldsymbol{\sigma} = nk_B T \mathbf{1} - \frac{k_B T n^2 d^3}{2} \int dS \hat{\mathbf{r}} \hat{\mathbf{r}} g(\hat{\mathbf{r}}). \quad (4)$$

Here,  $g(\hat{\mathbf{r}})$  accounts for the probability of collisions across the total internal contact area of the particles [36]. The relation (4) lends itself to an efficient evaluation-scheme in event driven simulations [37]. To resolve the local contact values  $g(\hat{\mathbf{r}})$ , the collisions can be recorded to yield:  $g(\hat{\mathbf{r}}) = 1/(2\pi n d^2 N k_B T) \times (1/\tau_c) \sum_{coll.} |\Delta \mathbf{p}(\hat{\mathbf{r}})|$ , with the sum of the magnitudes of the momentum transfers in binary particle encounters in direction  $\hat{\mathbf{r}}$  in the time-interval  $\tau_c$  [38]. Figure 4 shows the angle dependent contact value  $g(\hat{\mathbf{r}})$  which is consistent with our experimental findings (data not shown); the angle starts from the flow-axis. Curves for different strains are shown. In the linear regime, where  $\sigma_{xy} = G_\infty \dot{\gamma}_s$  holds, the local distortion exhibits the expected quadrupolar angular dependence. The contact probability decreases in the extensional and increases in the compressional direction. This behavior initially grows with strain. Beyond the linear regime, the isotropic distortion develops and matches the quadrupolar dependence in magnitude; the latter varies non-monotonously and follows the stress overshoot [31, 32]. In the stationary state, the contact probabilities are increased above the quiescent value for all angles. Even in the extensional direction, particles are pushed together by the shear flow. This is accompanied by a strong (monotonic) rise in the flow-dependent

pressure (not shown), because of the very low compressibility of the system at the high packing fraction. Microscopic MCT calculations in two dimensions which extend the work in Ref. [39] are included as inset in Fig. 4 and exhibit the non-monotonic behavior in the quadrupolar contribution but neglect an isotropic contribution [27].

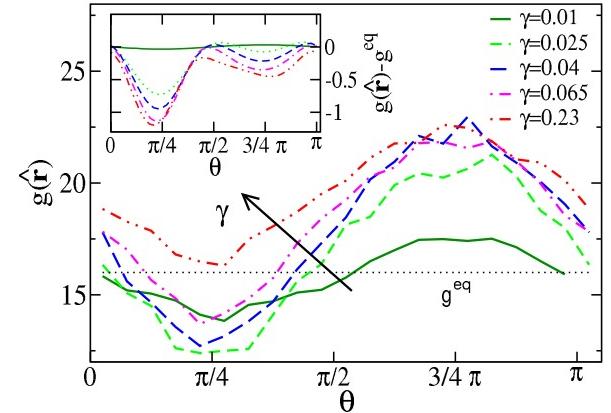


FIG. 4. Contact value  $g(\hat{\mathbf{r}})$  as a function of angle  $\theta$  to the shear flow direction from Brownian dynamics simulations of a binary disk mixture in  $d = 2$  at  $Pe \gg 1$ . An arrow indicates increasing strains as labeled; the black dotted line shows the equilibrium value. The inset shows corresponding MCT results for hard disks where an isotropic term is neglected [27].

In conclusion, we have shown that bulk metallic glasses close to their glass transition temperature and colloidal dispersions close to their glass transition packing fraction exhibit equivalent stress-strain relations when properly rescaled. Stresses agree when scaled by an entropic term characteristic for repulsive interactions; it is proportional to the thermal energy per particle volume. Furthermore, strains agree when geometrical factors arising from the rheometer are accounted for, and shear rates agree when properly rescaled by the quiescent internal relaxation time. Initially, stress increases linearly with strain, but for large Weissenberg numbers, when the external rate exceeds the inverse internal relaxation time, an overshoot originates due to negative stress autocorrelations. A schematic model of MCT rationalizes the rescaled curves with comparable parameters for metallic and colloidal systems. The microscopic origin of this effect is investigated by microscopy, simulations and microscopic MCT. The quadrupolar distortion expected from continuum elasticity theory, dominates only during the linear regime. In the nonlinear regime, a strong rise in an isotropic distortion arises from the constraints of local packing. It corresponds to a local compression under flow and causes a monotonous increase in the pressure.

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